

AgCuVO₄: a quasi one-dimensional $S = 1/2$ chain compound

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We present a joint experimental and computational study of the recently synthesized spin $1/2$ system silver-copper-orthovanadate AgCuVO₄ [A. Möller and J. Jainski, Z. Anorg. Allg. Chem. **634**, 1669 (2008)] exhibiting chains of *trans* corner-sharing [CuO₄] plaquettes. The static magnetic susceptibility and specific heat measurements of AgCuVO₄ can be described to a good approximation by the Bonner-Fisher spin-chain model with $J_{\text{intra}} \approx 330$ K. Evidence for a Néel type of order at ~ 2.5 K is obtained from the specific heat and corroborated by ESR studies. To independently obtain a microscopically based magnetic model, density functional electronic structure calculations were performed. In good agreement with the experimental data, we find pronounced one-dimensional magnetic exchange along the corner-sharing chains with small inter-chain couplings. The difference between the experimentally observed and the calculated ordering temperature can be assigned to a sizable inter-chain frustration derived from the calculations.

I. INTRODUCTION

The quest for materials that form quasi one-dimensional magnetic subunits has evolved into an important part of modern solid-state physics and chemistry over the last one or two decades.¹ Concerning quasi one-dimensional spin chains, the fundamentally different behavior of systems of even- and odd spin numbers has been one of the most spectacular theoretical findings by Haldane already in 1983.² In subsequent years it was realized that a large variety of exotic ground states and different unconventional elementary excitations are realized in low-dimensional quantum $S = 1/2$ systems, in many cases due to frustration effects. In particular, the ground state properties of a $S = 1/2$ chain with nearest and next-nearest neighbor interactions were calculated by Bursill *et al.*³ with the result of a spiral spin-order, depending sensitively on the ratio of the interaction parameters J_{ij} of the corresponding Heisenberg Hamiltonian

$$\hat{H} = \sum_{\langle ij \rangle} J_{ij} \hat{S}_i \hat{S}_j. \quad (1)$$

On the experimental side, the field of low-dimensional quantum magnetism has recently seen a considerable impetus from another subject of research activity, namely multiferroicity.⁴ Naito *et al.*⁵ found that the spiral spin order of $S = 1/2$ chains in LiCuVO₄ is able to induce a ferroelectric polarization at temperatures below ≈ 2.4 K. A similar behavior has been observed for LiCu₂O₂.⁶ The appropriate magnetic model^{7,8,9,10} and the theoretical description of this phenomenon has been controversially discussed in the literature recently, from both a phenomenological¹¹ and microscopical point of view.^{12,13}

In order to gain further insight into the phenomena and mechanisms at work, it is important to study similar systems with comparable characteristics. From a structural point $S = 1/2$ chains of interlinked [CuO₄] plaquettes may connect via edges or corners. Whereas the latter systems show typically antiferromagnetic nearest neighbor

(NN) couplings, the edge-shared systems (i.e. LiCuVO₄, LiCu₂O₂) exhibit either ferro- or antiferromagnetic NN couplings according to their Cu-O-Cu bond angles close to 90° in agreement with the Goodenough-Kanamori-Anderson rules.¹⁴ A further structural feature is whether the [CuO₄] plaquettes of the chain are all orientated in a co-planar or corrugated/buckled fashion. This will significantly affect the intra-chain exchange parameters J_{intra} as well. For example, for the (planar) chain system Sr₂CuO₃ of corner-sharing [CuO₄] plaquettes one finds a pronounced contribution J_{NNN} from next-nearest neighbors (NNN) with $J_{\text{NN}}/J_{\text{NNN}} \approx 25$.¹⁵

Furthermore, the influence of inter-chain interactions needs to be considered and evaluated especially in the very low temperature regime. Thereby, a classification of the one-dimensional systems regarding their magnetic properties may be achieved, e.g. Spin-Peierls transition (dimerised model) or magnetically ordered exhibiting either classical Néel or spiral spin order, respectively.

In this paper, we present a combined experimental and theoretical study of the $S = 1/2$ chain compound AgCuVO₄ (Fig. 1), which was synthesized recently.¹⁶ A classification of this system only based on its crystal structure is far from obvious: Whereas the [CuO₄] plaquettes in AgCuVO₄ form corner-shared chains, the Cu-O-Cu bond angles are rather close to the typical angles in edge-shared cuprate chains. Our combined approach shows consistently that AgCuVO₄ can be described as a quasi one-dimensional $S = 1/2$ NN-only Heisenberg chain in very good approximation.

II. METHODS

Powder samples of AgCuVO₄ were synthesized by solid state reactions of CuO and α -AgVO₃ (obtained from Ag₂O and V₂O₅) at 700 K in alumina crucibles in air. Powder pellets were pressed using a self-made molding press and sintered for several days at 700 K. These samples were then used for measurements of the physical

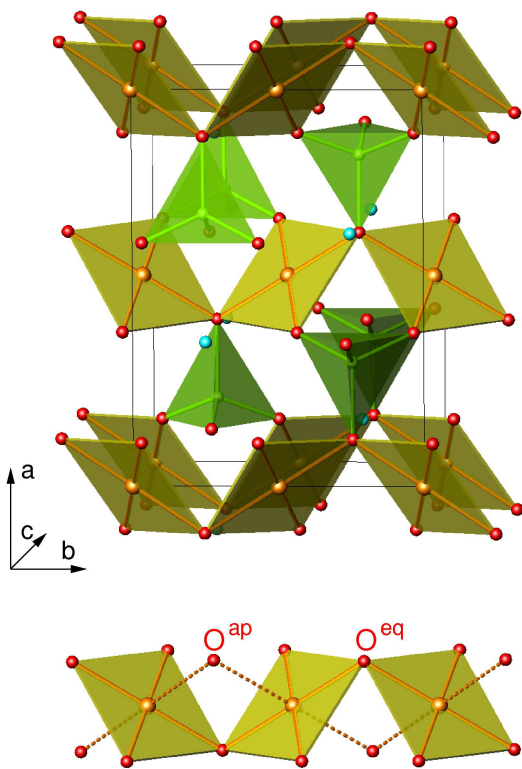


FIG. 1: (Color online) Top: Crystal structure of AgCuVO_4 . Green: $[\text{VO}_4]$ tetrahedra. Yellow: $[\text{CuO}_4]$ distorted square-planar entities. Light blue: Ag atoms. Bottom: Chain-like connectivity of the $[\text{CuO}_4]$ units in AgCuVO_4 . (Cu-O^{eq} (bold lines), Cu-O^{ap} (dotted lines))

properties. The phase purity of all samples was checked by powder X-ray diffraction. Low temperature X-ray diffraction patterns were measured on a Stoe & Cie. diffractometer equipped with a closed-cycle Helium cryostat (Lake Shore) using $\text{Cu-K}\alpha$ radiation between 20 and 293 K. All measured diffraction patterns could be indexed and refined in the space group $Pnma$ discussed below, revealing no structural transition in the investigated range.

The static magnetic susceptibility of AgCuVO_4 was measured in external magnetic fields of 0.1 T and 0.5 T in field-cooled (fc) and zero-field-cooled (zfc) mode (SQUID magnetometer; MPMS, Quantum Design).

The electron spin resonance (ESR) measurements were performed at X-band frequencies ($f = 9.4$ GHz) using a standard spectrometer together with a He-flow cryostat that allows to vary the temperature from 2.6 to 300 K. ESR probes the absorbed power P of a transversal magnetic microwave field as a function of a static and external magnetic field B . To improve the signal-to-noise ratio, we used a lock-in technique by modulating the static field, which yields the derivative of the resonance signal dP/dB .

The heat capacity was determined on the same sample by a relaxation-type method ($m \approx 11$ mg; PPMS, Quan-

tum Design) in external magnetic fields of 0, 3, 6, and 9 T.

For the electronic structure calculations the full-potential local-orbital scheme FPLO (version: fplo7.00-28) within the local (spin) density approximation (L(S)DA) was used.¹⁷ In the scalar relativistic calculations the exchange and correlation potential of Perdew and Wang was chosen.¹⁸ To consider the strong electron correlations for the Cu^{2+} ($3d^9$) configuration, we use the LSDA+ U ¹⁹ approximation varying U_d in the physically relevant range from 6 – 8.5 eV. The LDA results were mapped onto an effective tight-binding model (TB) and subsequently to a Hubbard and a Heisenberg model.

III. CRYSTAL STRUCTURE

Fig. 1 shows a perspective view of the crystal structure of AgCuVO_4 . The compound crystallizes in the orthorhombic space group $Pnma$ with lattice parameters $a = 9.255(1)$ Å, $b = 6.778(1)$ Å and $c = 5.401(1)$ Å, as determined by single crystal X-ray diffraction at room temperature.¹⁶ Isolated $[\text{VO}_4]$ tetrahedra (containing 'nonmagnetic' V^{5+}) are connected to the Cu^{2+} ions as bridging complex ions within the chain as well as between neighboring chains of *trans* corner-sharing $[\text{CuO}_4]$ plaquette entities along the b axis. These chains are furthermore separated from each other by isolated, nonmagnetic Ag^+ ions, also shown in Fig. 1. A more detailed description of the crystal structure is given by Möller *et al.*¹⁶

The magnetic Cu^{2+} ions ($S = 1/2$) are coordinated by four oxygen atoms in a square-planar fashion with a typical average Cu-O^{eq} distance of 1.995 Å, whereas the distance to the two apical oxygen atoms (O^{ap}), designated by dotted lines in Fig. 1, is 2.511(4) Å. Considering the elongated octahedral coordination of Cu^{2+} a $d_{x^2-y^2}$ ground state character can be assumed. The bridging angle $\angle(\text{Cu-O}^{\text{eq}}\text{-Cu})$ within the chains is $113.0(2)^\circ$, indicative of predominantly antiferromagnetic interactions of the spins according to the Goodenough-Kanamori-Anderson rules.¹⁴ Although Fig. 1 suggests an edge-sharing connectivity within the chains, the effective exchange via the apical oxygen atom (O^{ap}) is almost negligible, since the related d_{z^2} is fully occupied. Any superexchange via O^{ap} would be expected to give a ferromagnetic coupling in relation to the bridging angle ($\text{Cu-O}^{\text{ap}}\text{-Cu}$) of 85° . Therefore, one might consider this system as a quasi one-dimensional $S = 1/2$ antiferromagnet build of *trans* corner-sharing $[\text{CuO}_4]$ plaquettes. However, it should be noted that AgCuVO_4 is not isotypic with LiCuVO_4 which contains edge-sharing $[\text{CuO}_4]$ plaquette entities. Thus, distinct differences with respect to the magnetic interaction pathways associated with the Cu^{2+} $d_{x^2-y^2}$ ground state occur.

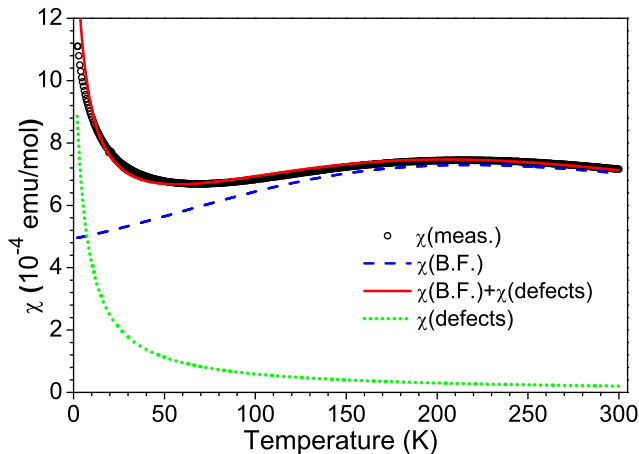


FIG. 2: (Color online) Temperature dependence of the static magnetic susceptibility of AgCuVO_4 (0.1 T, fc), black circles. $\chi(\text{B.F.})$ gives the result for an isotropic chain (Bonner-Fisher model, dashed blue line) and $\chi(\text{defects})$ present the impurity contribution, dotted green line. The total fit is given by the red line.

IV. RESULTS AND DISCUSSION

A. Magnetic susceptibility

The temperature dependence of the static magnetic susceptibility measured in a field of 0.1 T in fc mode is plotted in Fig. 2. The broad maximum in $\chi(T)$ at around 200 K is a typical feature of a low-dimensional magnetic system. Towards lower temperatures, below approximately 50 K, a sharp upturn in the form of a 'Curie-tail' occurs, which most probably originates from paramagnetic impurities. Measurements at 0.1 T and 0.5 T showed identical behavior in fc and zfc mode (not shown here). At higher temperatures, the magnetic susceptibility $\chi(T)$ can be described according to the isotropic one-dimensional $S = 1/2$ model of Bonner and Fisher²⁰ using the spin-spin Hamiltonian in the form of $\hat{H} = J_{\text{intra}} \sum \hat{S}_i \hat{S}_{1+i}$. A magnetic coupling constant of $J_{\text{intra}}^x \approx 335 \text{ K}$ is derived for AgCuVO_4 , see dashed blue line in Fig. 2. We used a typical constant value for the g -factor ($g_{\text{average}} \approx 2.10$) for the determination of J_{intra}^x within the isotropic Heisenberg model. At low temperatures the magnetic contribution of defects becomes evident. Including 1.5 % paramagnetic $S = 1/2$ impurities (defects, dotted green line) with a Weiss temperature of $\Theta_{\text{imp}} \approx -5 \text{ K}$ we obtain a fit in good agreement with the experimental data for the temperature range from 10 to 300 K (red line of Fig. 2).

The effective antiferromagnetic coupling indicates a dominant $d_{x^2-y^2}$ ground state character of the Cu^{2+} ion in agreement with a superexchange path via the bridging oxygen atoms O^{eq} with an angle of 113° in this case. Of course, this highly oversimplified picture relating to

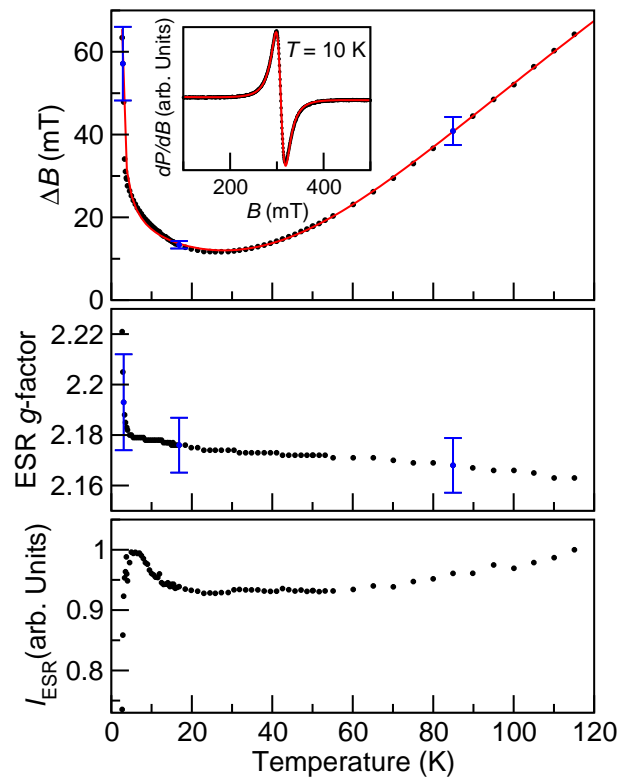


FIG. 3: (Color online) The inset shows a typical ESR signal (black circles) with a Lorentzian fit (red line) given. The temperature dependence of the signals line width (black circles) and a fit with Eq. 2 to the data (red line) is shown for AgCuVO_4 in the top main panel. The two lower panels show the temperature dependence of the g -factor (middle) and the intensity of the ESR signal (bottom panel) for AgCuVO_4 .

structural arguments calls for a more detailed analysis based on specific heat, ESR measurements and LDA calculations.

B. Electron spin resonance

Fig. 3 shows a typical ESR signal at $T = 10 \text{ K}$ (inset) and the temperature behavior of the line width (top panel) for AgCuVO_4 . At temperatures $T > 4 \text{ K}$ we observe a well defined signal which could be nicely fitted with a single Lorentzian line (red line in inset) providing the ESR parameters line width ΔB and g -factor ($g = h\nu/\mu_B B_{\text{res}}$, B_{res} - resonance field). Below 4 K an additional signal with a twice larger line width and nearly the same resonance field occurs. This second signal might be related to the anisotropy of the ESR parameters, but could also originate from impurities or indicate a resonance mode resulting from an antiferromagnetic ordered state.

In the two lower panels in Fig. 3 the temperature behavior of the ESR intensity and the measured g -factor is shown. The observed g -values of $\approx 2.17(1)$ are typical

for Cu^{2+} in a distorted octahedral environment and in fair agreement with the static susceptibility fitted by the Bonner-Fischer model. Above 10 K the intensity follows the magnetic susceptibility $\chi(T)$ (see Fig. 2) reproducing the broad minimum around 40 K. Below $T = 4$ K the ESR intensity reduces rapidly towards lower temperatures indicating a magnetic ordering below 4 K. A similar behavior above T_N is observed in the spin chain compound CuSiO_3 .²¹

The divergence of the g -factor and the line width at low temperatures also indicate a magnetic phase transition below 4 K. The temperature dependence of the line width $\Delta B(T)$ is comparable with that of LiCuVO_4 ²² and CuGeO_3 ²³ showing a pronounced minimum between 10 and 40 K. We fitted $\Delta B(T)$ with a classical critical divergence at T_N (first term in Eq. (2) below) and an empirical expression for the high temperature part.²³ (second term in Eq. (2)):

$$\Delta B = C \left(\frac{T}{T_N} - 1 \right)^{-p} + \Delta B(\infty) \exp \left(-\frac{C_1}{T + C_2} \right) \quad (2)$$

C , p , T_N , $\Delta B(\infty)$, C_1 , and C_2 are treated as 6 fitting parameters. Table I summarizes the fit results.

TABLE I: Fit parameters according to equation (2) for the line width of the ESR signals for AgCuVO_4

C (mT)	p	T_N (K)	$\Delta B(\infty)$ (mT)	C_1 (K)	C_2 (K)
35 ± 0.7	0.35 ± 0.05	2.5 ± 0.2	294 ± 50	199 ± 30	6 ± 5

The fit results on the first term in Eq. (2) depend only weakly on the parameters of the second term and vice versa. This holds especially for T_N . The influence of the other parameters is included in the uncertainty displayed in Table I.

C_1 is related to the order of magnitude of the isotropic exchange constant, because the parameter indicates the transition from the strongly correlated one-dimensional regime at low temperatures $T \ll J_{\text{intra}}$ to the purely paramagnetic regime $T \gg J_{\text{intra}}$. C_2 indicates the influence of the low-temperature phase transition (long-range magnetically ordered phase) on the line broadening. It is necessary to recall that this purely empirical parametrization has no underlying microscopic picture. Nevertheless, the ESR corroborates the antiferromagnetic ground state and the onset of long-range order setting in at ≈ 2.5 K (see section on the specific heat capacity below).

C. Specific heat capacity

Inset A of Fig. 4 shows the measured specific heat capacity, $C_p(T)$, in zero field for AgCuVO_4 below 320 K. The field dependence of $C_p(T)$ is given in the main panel of Fig. 4. Below 3 K an anomaly is clearly visible in lower

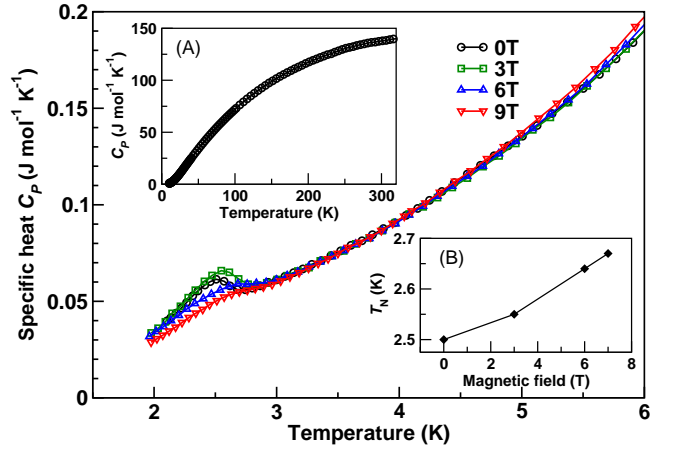


FIG. 4: (Color online) Temperature dependence of the specific heat of AgCuVO_4 for different magnetic fields. Inset (A): Large temperature range in zero field. Inset (B): Field dependence of the Néel temperature.

fields, which broadens and smears out with increasing field. The field dependence indicates that this effect can be attributed to an antiferromagnetically ordered ground state. The shift of the the Néel temperature with increasing field from 2.5 K to almost 2.7 K is shown in the inset (B) of Fig. 4. We have fitted $C_p(T)/T$ versus T^2 below 10 K (Fig. 5) to Eq. (3) in order to obtain the coefficients (γ and β_1) related to the magnetic ($C_m(T)$) and lattice ($C_l(T)$; harmonic lattice approximation) part of the specific heat.

$$C_p(T)/T = \gamma + \beta_1 T^2 + \beta_2 T^4 \quad (3)$$

The lattice contribution (phonons) is associated with $\beta_1 = 0.34(5) \text{ mJ mol}^{-1} \text{ K}^{-4}$ and allows an estimate of the Debye temperature $\Theta_D = (12\pi n N_A k_B / 5\beta_1)^{1/3} \approx 342 \text{ K}$, a typical value for $[\text{CuO}_{4/2}]$ compounds with edge-sharing connectivity.²⁴ The value of $\beta_2 = 0.00234(4) \text{ mJ mol}^{-1} \text{ K}^{-6}$ is of the expected magnitude ($\approx 1\% \beta_1$). The magnetic part of the specific heat is presented by $\gamma = C_m/T$. $C_m(T)/T$ is found to be almost constant at low temperatures for an isotropic $S = 1/2$ chain and related to the magnetic exchange parameter, $J_{\text{intra}} = 2N_A k_B / (3C_p^{(T \rightarrow 0)}/T)$.²⁵ With $\gamma = 16.9(1) \text{ mJ mol}^{-1} \text{ K}^{-2}$ we find within the Heisenberg model $J_{\text{intra}}^{C_p}$ of $\approx 330 \pm 10 \text{ K}$ in excellent agreement with the value derived from the fit to the susceptibility data.

The long-range order setting in below 3 K occurs from inter-chain couplings and the Néel temperature, T_N , associated with this transition can be used to estimate the exchange parameter $J_{\text{inter}}^{C_p}$ of $\approx 0.75 \text{ K}$ from Eq. (4)²⁶

$$J_{\text{inter}} = T_N / (1.28 \sqrt{\ln(5.8 J_{\text{intra}} / T_N)}) \quad (4)$$

In principle the same result is obtained from a more recent theoretical approach²⁷ to estimate the inter-chain

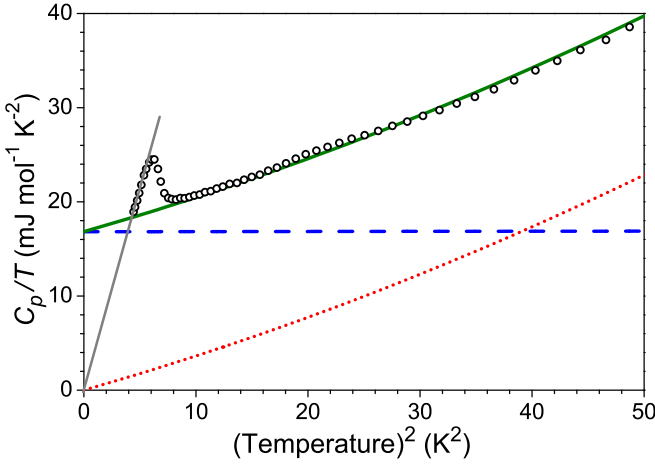


FIG. 5: (Color online) Magnetic heat capacity C_p/T at zero field versus T^2 (black circles) for AgCuVO_4 including the fit to equation (3) (green line) as well as C_m/T (dashed blue line) and C_L/T (dotted red line). The grey line presents a linear fit below T_N , see text.

coupling from T_N . Here, the intra-chain coupling parameters J_{intra} derived from $C_p(T)$ and $\chi(T)$ data are not only consistent but almost identical. Furthermore, J_{intra} is found to be ≈ 440 times larger than J_{inter} . Therefore, AgCuVO_4 can be regarded as a quasi one-dimensional $S = 1/2$ system at $T \gg 3\text{ K}$. For a more detailed analysis and evaluation of J_{inter} in this case see section on the electronic structure below.

In Fig. 5 a linear fit below T_N ($T^2 < 5.5\text{ K}$) is included. The extrapolated intersection with the origin is in agreement with the insulating properties of AgCuVO_4 and reveals the magnon contribution to the total specific heat capacity, C_p , which follows approximately a T^3 law typical for an antiferromagnet.

D. Electronic structure

To gain microscopic insight into the electronic and magnetic properties of the system we carried out band structure calculations based on density functional theory (DFT) and subsequent model calculations.

In Fig. 6 the obtained density of states (DOS) of the valence states with a band width of about 6 eV is shown. This band width is rather typical compared with other cuprates revealing a chain-type of structural feature like CuGeO_3 ²⁸ or Sr_2CuO_3 ¹⁵. The valence band is dominated by Ag, Cu and O states. The quite narrow Ag 4d contribution between -2 eV and -0.5 eV indicates a Ag^+ cation. For Cu and V the calculations yield magnetic Cu^{2+} and non-magnetic V^{5+} as could be expected from the crystal structure in terms of their coordination spheres (see Fig. 1): Cu and O form strongly distorted $[\text{CuO}_6]$ octahedra with considerably shorter Cu-

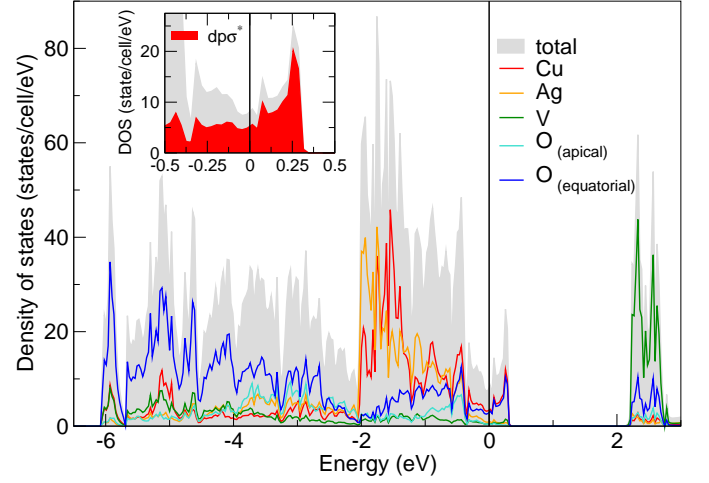


FIG. 6: (Color online) Calculated total and atom resolved density of states for AgCuVO_4 . The Fermi level is at zero energy. Inset: Orbital-resolved density of states for the $dp\sigma^*$ states of the antibonding half-filled band.

O^{eq} bonds in the equatorial plane leading to the characteristic $[\text{CuO}_4]$ plaquettes, whereas the non-magnetic V^{5+} is tetrahedrally coordinated, $[\text{VO}_4]$. Magnetically active V^{4+} usually appears in drastically distorted coordination spheres (e.g. square-pyramidal).

As a consequence of the Cu^{2+} state the anti-bonding Cu-O $dp\sigma^*$ states of the system are half filled. Corresponding to the 4 Cu per unit cell, four half-filled bands cross the Fermi energy ε_F (see Fig. 7) in our LDA calculation. This metallic solution is in contradiction to the insulating character of the compound concluded from the red color of the crystals and a well known shortcoming of the LDA calculations. As LDA underestimates the strong correlations of the Cu^{2+} ($3d^9$) configuration, these missing correlations can be taken into account by mapping the relevant LDA bands onto a TB model and subsequently onto an Hubbard and Heisenberg model. Alternatively the strong Coulomb repulsion in the Cu3d shell can be considered explicitly in a mean-field like approach using the LSDA+ U scheme.

In many cuprates the anti-bonding $dp\sigma^*$ states are well separated from the lower-lying valence states, while in AgCuVO_4 these states overlap with the lower lying part of the valence due to a sizable admixture of other orbitals. The inset of Fig. 6 shows the orbital-resolved DOS of the Cu-O $dp\sigma^*$ states in comparison with the total DOS. In the region between ε_F and 0.25 eV the $dp\sigma^*$ states clearly dominate the antibonding bands, whereas from ε_F to -0.5 eV contributions from other orbitals increases notably. Accordingly, the hybridization with lower lying parts of the valence band is also visible in the upper panel of Fig. 7 where the band characters of the $dp\sigma^*$ states spread out to lower energies (mainly around Γ and X).

The sizable admixture of other valence states to the antibonding bands that are responsible for the magnetic

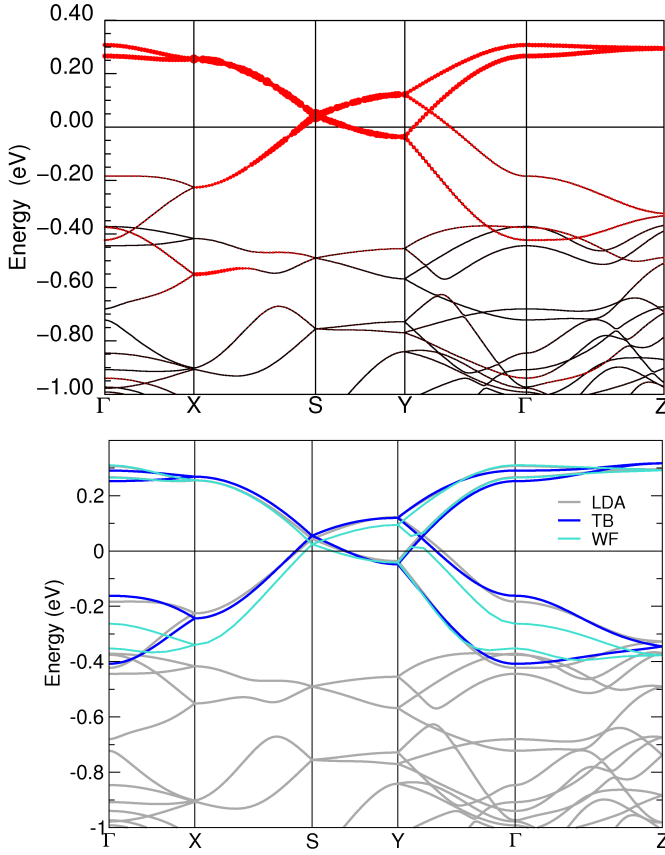


FIG. 7: (Color online) Antibonding $dp\sigma^*$ bands from the LDA calculations together with the band from a direct tight binding (TB) fit and from a Wannier function (WF) based mapping.

interactions in the system impedes a straight forward mapping to an effective one-band TB model using a least square fit procedure. The ambiguousness in the selection of the relevant bands, especially between Γ and X and Γ and Z , respectively, can be removed applying the Wannier function technique (see Fig. 9). The resulting leading transfer terms for both approaches are sketched in Fig. 8 and the values are given in Table II. The corresponding bands are highlighted in Fig. 7 (lower panel) on top of the LDA band structure. It can be clearly seen that in the upper part the least square TB fit and the Wannier function derived bands nearly coincide, while for the lower lying region with stronger admixture (see inset Fig. 6) both approaches show sizable deviations. This is mostly reflected in the leading nearest neighbor (NN) transfer integral t_1 , whereas the much smaller coupling to further neighbors are mostly unaffected. On the other hand, the good agreement between both methods justifies the application of an effective one-band picture.

From our mapping, we obtain a clear physical picture for the relevant interactions in the system: We find weakly interacting chains along the b direction with essentially only NN coupling t_1 (see Table II). Consistent

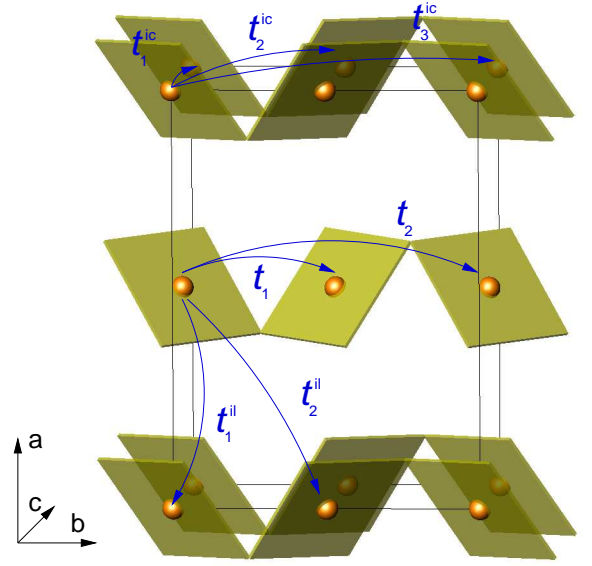


FIG. 8: (Color online) Sketch of the TB model for AgCuVO_4

TABLE II: Leading coupling terms for AgCuVO_4 from TB and WF approach.

t_i/meV	t_1	t_2	t_1^{ic}	t_2^{ic}	t_3^{ic}	t_1^{il}	t_2^{il}
$t_i(\text{TB})$	-145	2	17	7	6/-19	-16	-11/0
$t_i(\text{WF})$	-157	0	18	6	5/-20	-13	-10/3

with the Cu-O-Cu bond angle of about 113° this leading transfer is closer to the values for edge-shared chain geometry (e.g. CuGeO_3 ²⁸, Cu-O-Cu bond angle of about 99° , $t_1 \approx 175 \text{ meV}$) than for the couplings of the corner-shared chains (e.g. Sr_2CuO_3 ¹⁵, Cu-O-Cu bond angle of 180° , $t_1 \approx 410 \text{ meV}$). This vicinity to the edge-shared chain compounds raises the question of the relevance of ferromagnetic contributions to the NN exchange J_1 . Mapping the TB model via a Hubbard to a Heisenberg model (in the limit of strong correlations and at half filling) to describe the low lying magnetic excitations only yields the antiferromagnetic parts $J_i^{\text{AF}} = 4t_i^2/U_{\text{eff}}$ of the total exchanges J_i . The ferromagnetic contributions can be estimated comparing the TB derived exchange J_i^{AF} with the result of LSDA+ U calculations for magnetic super cells. Using a standard one-band value $U_{\text{eff}} = 4 \text{ eV}$ ²⁸ we obtain for the NN exchange $J_1^{\text{AF}} = 23 \pm 3 \text{ meV}$ ($265 \pm 35 \text{ K}$).³³ For the calculated range of physically relevant U_d values³⁴ in the LSDA+ U approach we obtain $J_{\text{intra}}^{\text{TH}} \equiv J_1 = 24 \pm 3 \text{ meV}$ ($280 \pm 35 \text{ K}$). The very good agreement between J_1^{AF} and $J_{\text{intra}}^{\text{TH}}$ leads us to the conclusion that ferromagnetic contributions to the NN exchange in AgCuVO_4 are basically negligible. The choice of U_d is additionally justified by the resulting gap size of $1.5\ldots 2 \text{ eV}$ consistent with the red color of the sample and in agreement with measurements of the absorption in the visible part of the electromagnetic spectrum at sig-

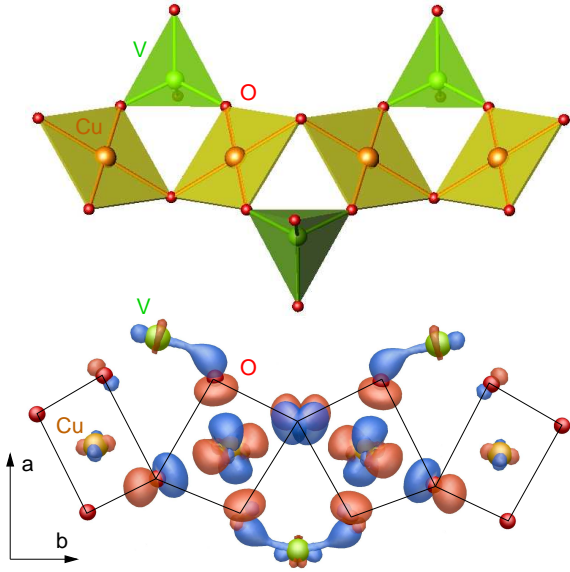


FIG. 9: (Color online) Cu $3d_{x^2-y^2}$ related Wannier functions for a chain segment in AgCuVO_4 .

nificantly lower energy for AgCuVO_4 in comparison with $\alpha\text{-AgVO}_3$ (reported gap of $\approx 2.3\text{ eV}$)²⁹ as a reference.

A closer inspection of the effective exchange path by the calculated Wannier functions (see Fig. 9) shows that the interaction does not appear from a coupling via the shared O^{eq} only, but also involves states of the $[\text{VO}_4]$ tetrahedra. These contributions are in line with the picture obtained from the orbital resolved DOS (see Fig. 6 and inset) with additional states mixing into the antibonding $d\rho\sigma^*$ band.

It is well known that for ideal one-dimensional chains no magnetic order appears.³⁰ In our compound, we calculated inter-chain couplings $J_{\text{inter}}^{\text{TH}}$ of the order of $1/65$ with respect to the NN intra-chain exchange $J_1 = J_{\text{intra}}^{\text{TH}}$. The calculated exchange values allow the estimate of the ordering temperature T_N according to Eq. 4.²⁶ Using $J_1 = 24\text{ meV}$ (280 K) and an effective $J_{\text{inter}}^{\text{TH}} = 0.25\text{ meV}$ (3 K) as an average of the inter-chain couplings J_1^{ic} and J_3^{ic} in the crystallographic bc plane and the inter-layer exchanges J_1^{il} and J_2^{il} , see Fig. 8, we obtain a theoretical value $T_N^{\text{TH}} = 8.6(5)\text{ K}$ for the Néel temperature.

Compared to the experimentally observed $T_N = 2.5\text{ K}$ this is a clear overestimate by a factor of ≈ 3.5 . A closer inspection of the further magnetic interactions between chains belonging to different 'magnetic layers' separated by a diagonal component along the crystallographic a -direction (J^{il} , cf. Table II) reveals the frustrating nature of the leading inter-layer couplings J_1^{il} and J_2^{il} (compare Fig. 8 and see Fig. 10). Therefore, we can assign the deviation of the calculated and observed T_N to the latter considerable inter-chain frustration. The situation is comparable to the quasi 1D model compound Sr_2CuO_3 , where a similar suppression of the ordering temperature compared to the calculation

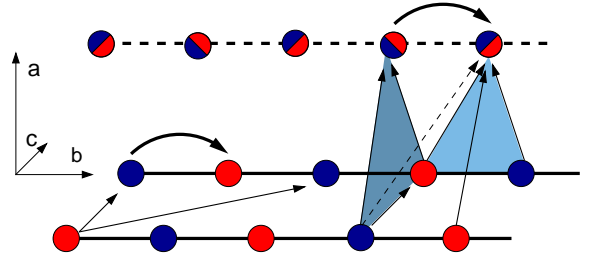


FIG. 10: (Color online) Sketch of the magnetic model for AgCuVO_4 . The leading inter-chain exchange terms yield unfrustrated coupling between the chains in the crystallographic bc plane, but sizable frustration between the layers (indicated by filled triangles). This is illustrated by the different colors (red, blue) for different spin directions according to the antiferromagnetic nature of the relevant exchange couplings.

appears.¹⁵ The strong influence of frustration on the ordering temperature is especially pronounced for the compound $\text{Sr}_2\text{Cu}(\text{PO}_4)_2$, where the leading inter-chain couplings J_{\perp} are fully frustrated.³¹ Although the main couplings are comparable to AgCuVO_4 , the ordering temperature of $\text{Sr}_2\text{Cu}(\text{PO}_4)_2$ is smaller by a factor of about 30. The strong quantum fluctuation in quasi 1D spin $1/2$ compounds not only lead to a drastic reduction of the ordering temperature, but also to a small ordered moment. Using the same exchange parameters as for the calculation for T_N we predict an ordering moment of about $0.15\ \mu_B$ (Eq. 7 in Ref. 26).

In conclusion, our band structure calculations provide us with a picture (see Fig. 10) of quasi-1D NN Heisenberg chains with small inter-chain couplings where the in-plane couplings J^{ic} support AFM order, whereas sizable inter-layer frustration J^{il} impedes AFM.

V. SUMMARY AND CONCLUSIONS

We have presented measurements of the static magnetic susceptibility and the specific heat capacity, which evidence the pronounced one dimensional magnetic properties of AgCuVO_4 related to structural features and to the $d_{x^2-y^2}$ ground state character of the Cu^{2+} ion. Within the isotropic exchange model for a Heisenberg system $J_{\text{intra}} \approx 330\text{ K}$ has been derived from the experimental data. Furthermore, weak inter-chain coupling is evident from specific heat capacity and ESR measurements leading to a magnetically ordered state at $T_N = 2.5\text{ K}$. In order to gain insight into the magnetic interactions on a microscopic basis we performed full-potential electronic structure calculations. Subsequently derived Heisenberg models based on Wannier functions and LSDA+U calculations confirm the quasi 1D behavior. We found the main exchange along the chain $J_{\text{intra}}^{\text{TH}} = 280 \pm 35\text{ K}$ in good agreement with the thermodynamic measurements and several small inter-chain couplings leading to an estimate for the antiferro-

magnetic ordering temperature $T_N^{\text{TH}} \sim 8.6$ K. From the magnetic model (see Fig. 10) the overestimate of T_N^{TH} by a factor of 3.5 compared to the experimental observed ordering temperature can be attributed to frustrated inter-chain couplings along the crystallographic a direction. All inter-chain couplings are fairly weak and according to our experimental data and calculations neither spiral order and subsequent multiferroic behavior nor a Spin-Peierls transition is expected for AgCuVO_4 . Moreover, this compound with effective NN couplings of the order of room temperature can be classified as 'in between' edge- and corner- shared chains and might serve as a good candidate to study the characteristic properties of a one-dimensional $S = 1/2$ Heisenberg system also by other complementary methods in temperature ranges that are experimentally easier accessible. In particular,

single crystals are highly desirable for further investigation of the thermal transport and expansion behavior as well as for studies of the ordered magnetic moment and the magnon dispersion by neutron diffraction.

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 - ³⁴ Within the range of $U = 6...8.5$ eV we obtain agreement with the experimentally reported exchange integrals for a large number of edge- and corner-shared cuprate systems.